PYROGENICS, INC.

A Study of the Use of Vapor and Vacuum
Deposition Technique For The Development
Of High Strength Filamentary Materials

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Introduction:

Considerable research effort has been expended in recent years on the development of refractory high strength filamentary materials. Such materials when produced by evaporative or vapor conversion methods, have shown great promise, but have either not been dimensionally continuous, or have been limited in their strengths by the natures of the continuous substrates upon which they have been deposited.

Extremely high strength graphite whiskers of limited length have been generated via sublimation from a carbon arc by R. Bacon[1], and gas reaction graphite whiskers of similar geometric limitations and lower strengths have been produced by Meyer[2] and by Papaleges and Bourdeau[3]. Gas reaction coatings of pyrolytic graphite have been deposited on graphite yarns by Higgs[4] et al, Papalegis[3] and others, but the irregularities of the substrate surfaces have limited the product strength. Strong, extremely flexible sheet filaments of pyrolytic graphite have been produced by Robba[5], but these have yet to be generated in continuous form in thicknesses which will optimize strength.

Silicon carbide whiskers, produced by gas conversion, have possessed high strength, but have been non-uniform in physical properties and of limited lengths[6].

This contract was initiated with a thorough survey of literature pertaining to synthesis, treatment and properties of pyrolytic materials.

Surveillance of this literature has indicated that the strengths of whiskers coatings and massive pyrolytic graphite deposits have been strongly influenced by three parameters:

1. Substratum Surface.

2. Specimen Thickness.

3. Subsequent Treatment (i.e. annealing, hot and cold work)

Smooth substratums, thin deposits, and good orientation through treatment should provide an optimum pyrolytic filament. This program will consider these three parameters in the development of high strength filaments.

Approach

Our approach to generation of high strength continuous materials is focused upon pyrolytic graphite synthesis techniques, with adaptation of these techniques to other material candidates, where such adaptation appears possible.

The approaches to be considered are:

1. Deposition upon a suitable liquid surface.

2. Deposition on other (solid) materials, i.e. rhenium, nickel, boron nitride, iridium.

3. Improvement of graphite substrate finishes prior to deposition, i.e. treatment of yarn.

4. Stress-growth of fibers or sheet by evaporative feeding.

5. Stress-strengthening of fibers.

I. Deposition Upon Liquid

The possible advantages to deposition upon a liquid surface are:

1. Ready shear of deposit from substrate for continuous withdrawal.

2. Thin film generation, made possible by ease of withdrawal.

3. Freedom of surface from gross imperfections.

4. By virtue of its superficial perfection, the liquid surface should be non-nucleating and may permit continuous growth from a single seed.

5. Freedom from stresses which would be introduced by a solid substratum.

Platinum was selected as the liquid surface upon which pyrolytic graphite deposition would be attempted. This selection was made for the following reasons:

1. Platinum is molten at graphite deposition temperatures.

2. Its vapor pressure is low at these temperatures.

3. It is not known to form carbides.

4. Its solubility for carbon is low.

The original feasibility attempts to deposit pyrolytic graphite on molten platinum consisted of heating a length of platinum wire in a narrow, resistance heated graphite boat. The boat, which was approximately 2-1/2 inches long, was heated between water cooled electrodes in a quartz vacuum chamber. Power input was controlled by a variable transformer, and pressure was measured by a Dubrovin vacuum gauge. Figure 1 shows the apparatus mounted in a glass rack. The platinum could not thus be heated above its melting point because, as it fused in contact with the boat, it shunted the current down its length. The low resistance of the platinum had prevented sufficient heat generation for achieving higher temperatures.

To correct this difficulty, the cavity in the boat was restricted to a shallow, 0.100" diameter blind hole. In such an arrangement, the platinum was heated by conduction of heat from the ends of the

boat. The platinum in a 0.100" length cavity could not shunt current over more than a 0.100" length of the boat, and this quantity of platinum was also insufficient to dissipate heat beyond our means to generate it.

During the first effective deposition run, methane at pressures ranging from 7.8 to 10.1 mm. was introduced to molten platinum which was at 2330°C. These conditions, maintained for one hour, demonstrated the feasibility of depositing pyrolytic graphite on molten platinum. The deposit was extremely irregular, suggesting that an excessively heavy film had been generated, permitting inherent stresses to distort the unrestricted deposit. Figure 2 shows this deposit on the platinum in the boat. Figure 3, at higher magnification, shows smooth, as well as irregular deposits.

Deposition at higher temperatures was attempted, but as the temperature was increased, the vapor pressure of the platinum became sufficient to generate a soot on parts of the chamber in line-of-sight with the metal.

Pyrolytic graphite deposition upon molten platinum from methane at 7.0 mm. was attempted at 1970°C for two minutes. A deposit was produced, about 0.0007 thick, a specimen of which was later consumed without ash residue in a 900°C air furnace, along with a control specimen of pyrolytic graphite. This, in conjunction with metallography of the specimen which showed the characteristic pyrolytic

structure, indicated the material was pyrolytic graphite. Figures 4 and 5 show the specimen with a wrinkled foil of deposit on the surface. Wrinkling was thought to be due to the liquid-to-solid contraction of the underlying platinum metal. Figure 6 shows the rippling of the surface layers of pyrolytic graphite which was sufficient to shear the deposit into two major and numerous minor layers, the latter estimated at 70×10^{-6} inches thick.

While melting a specimen of platinum prior to introduction of methane for pyrolytic graphite deposition, it was observed through the optical pyrometer that the platinum appeared to be emitting as much light as the surrounding graphite. This sudden increase in emissivity indicated that the platinum may already have been coated with graphite via mass transfer from the graphite boat. Methane was not introduced, and the specimen was subsequently examined. A very thin, glossy film was observed on the platinum surface. A portion of this film was peeled away, and upon exposure to increasing temperatures in an air furnace, was consumed without ash residue at about 900°C. The platinum specimen was examined metallographically, and a film was observed (in Figure 7) having the polarized lighting characteristics of graphite, but without the pyrolytic structure. This suggested that graphite was formed on the molten surface by precipitation of carbon which had been dissolved from the boat. It is believed that the thermal gradient from the bottom of the saturated melt to its surface induced this precipitation of non-pyrolytic graphite.

Other examples of this transfer also became apparent. Figure 8 shows a pyrolytic graphite-coated platinum specimen in its boat, with part of the pyrolytic graphite peeled away. The highly reflective smooth finish to this deposit had looked promising as an indication of relative freedom from gross imperfections. A microsection (Figure 9) of a coated portion of the specimen shows the additional feature of an underlying non-pyrolytic graphite film. Another example of this behavior is shown in Figure 6 and again in Figure 10, in which the two graphite films separated, either by virtue of platinum liquid-to-solid contraction upon cooling, or from growth of the pyrolytic layer. In Figure 10 the pyrolytic layer was quite uniform in thickness, whereas the underlying graphite layer was irregular. This suggested that the sublayer may have been partially dissolved by increasing temperatures due to insulation by the pyrolytic deposit. Crystals of graphite can also be observed in the platinum matrices, probably precipitated upon solidification of the melts.

An extreme example of this carbon transfer can be seen in Figure 11, where the colder portions of the melt during a much longer (one hour) run have become largely displaced by precipitated graphite. Figure 12 shows the progression of the melt into the hottest (center) zone of the

graphite boat. Dissolution of graphite in the hottest regions, followed by precipitation in colder regions is clearly illustrated. The difference in structure between pyrolytic and precipitated graphite is shown in Figures 13, 14 and 15, which are progressively magnified regions including and adjacent to an irregular outgrowth of pyrolytic graphite. The striated appearance of the pyrolytic graphite is contrasted with the untextured precipitated graphite in Figure 15.

Although platinum does not possess a high solid solubility for carbon, its liquid solubility appears quite high. This solution effect can introduce a solid sub-layer, from which a pyrolytic graphite deposit must be withdrawn, complicating the preferred model of continuous shearing of deposit from a liquid surface.

The liquid surface model which had been pursued for pyrolytic graphite deposition was re-examined for boron and silicon carbide deposition upon copper. Little solubility data was uncovered on the solubilities of boron or silicon carbide in molten copper, but indications were that solubilities were low or negligible.

Copper had been selected as the liquid medium, as the deposition temperatures, ranging from 1100°C to 1300°C, were high enough to exceed the melting point, and were low enough to avoid excessive copper vapor pressures. To avoid shunting of current by molten copper in a resistance heated boat, the copper was heated in a graphite boat

seated atop a graphite resistance element. (See Figure 16). Contact between the boat and the heating element was insufficient to produce shunting difficulties, but it was sufficient to heat the boat by radiation and conduction to the desired temperatures. This arrangement also minimized electromagnetic agitation of the copper which had occurred when it was heated directly in a resistance heated boat.

Attempts to deposit boron were carried out in the glass rack apparatus previously described. Boron tribromide was passed through the reaction chamber, admixed with a dried hydrogen carrier gas. The hydrogen was first passed over the heating element, boat and copper, until deposition temperatures were attained. The hydrogen was then valved through the liquid boron tribromide at one atmosphere and room (25°C) temperature, and passed over the heated copper, boat, and heating element.

In no case was any deposit observed upon the melt surface, although boron nodules were found at the edge of the melt. A hard, brittle coating, probably a carbide of boron, was found on the boat and heating element. This coating could be flaked easily from the graphite surface. The copper had apparently dissolved any boron which had been deposited upon the melt. An indication of this alloying was the wetting of the graphite surface by the copper in the immediate vicinity

of the melt, and the bronzed luster the copper had sustained.

Because of the alloying effect, the experiments in deposition of

boron on molten copper were halted.

The deposition of silicon carbide on molten copper was then

attempted. In the same experimental rig, hydrogen was passed

over the heating element, boat and copper until deposition tem-

peratures were reached at the metal surface. The hydrogen was

then bubbled through tetramehyl silane at 1 atm. and room tempera-

ture, to carry the silicon compound into the reaction chamber. At

1250°C and 1300°C a deposit was obtained on the molten copper.

This deposit was extremely friable and weak, indicating an absence

of structural continuity. Figure 17 shows the specimen with part

of the deposit flaked off. As can be seen, there was no wetting of

the boat by the molten copper. The heating element, which achieved

a temperature of 1700°C, had sprouted a zone of whiskers around its

mid-section. (See Figures 18 and 19), which tended to grow inward from

the cooler ends toward the mid-region. The whiskers themselves were

stiff and resilient, and possessed the vitreous blue-black appearance

often seen in silicon carbide crystals. In view of the work being done

elsewhere with silicon carbide whiskers[6] further probing of SiC

whisker growth phenomena was postponed until all the initial objectives

of the present program had been exhausted.

II Deposition Upon Solid

In order that solids be utilized as substrates in a continuous process of filament deposition, they should have excellent surface finishes and be unaffected by repeated exposure to the deposition environment.

One of the materials considered for this role was rhenium, as there was no record of rhenium carbides forming at 2000°C or above. A rolled ribbon of rhenium, 0.5" x .005" x 2-1/2" was vacuum resistance heated in the reaction chamber to 2000°C and methane was then admitted at 8 mm for two minutes. An extremely smooth glossy deposit with no adherence had formed over the metal. The underside of the deposit, which had been in contact with the strip, was reflective in its luster. (See Figure 20) The coating, which was quite brittle in its deposited state, was of fairly uniform thickness (See Figure 21), and had a pyrolytic graphite structure.

The rhenium strip had become extremely brittle and crazed as a result of this treatment. The brittleness, according to the supplier and the manufacturer, is a result of solid solution of carbon in contact with the metal surface. These results demonstrate that rhenium would not be satisfactory for repeated depositions of pyrolytic graphite, as envisioned in a continuous process of recirculating substratum ribbon or wheel.

Iridium, with a melting point of 2443°C and no known reactivity with carbon, may fulfill the role of high-finish solid substratum for continuous filament deposition. A ribbon of iridium is now being made up for this purpose.

Evaporative transfer of carbon to form a highly oriented fiber, or to feed stress-grown whiskers is one of the approaches outlined in the previous quarterly report (No. 1) of this contract. Prior to installation of suitable induction equipment, a simple arrangement was prepared in an attempt to achieve temperatures of 3000°C in the existing quartz chamber. Several difficulties were encountered which have limited the temperatures thus far attained, but the effort produced some interesting results. A preliminary experimental arrangement was made up, as shown in Figure 22. A graphite rod, concentric within a cylindrical graphite shield, was resistance heated between electrodes in the quartz chamber. The cylindrical shield was supported by boron nitride bushings, also concentric with the rod and cylinder, which insulated the shield from the heating element. At 2540°C a cemented joint burned out, terminating the run. The boron nitride bushings, on their surfaces facing the mid-point of the resistance element, were coated with deposits which had a graphitic appearance (Figure 23).

These deposits could not be scratched by a steel point, however, indicating that a carbide of boron had been generated. About 5% of this deposit was in the form of resilient whiskers (See Figure 24). It was reasoned that boron carbide was generated by the reaction of boron nitride and carbon, and that this product sublimed to form whiskers. This conclusion was stimulated in part by the work being performed by Gatti, et al[7] who have formed boron carbide whiskers by sublimation. In view of this work already being pursued, experiments in generating more boron carbide whiskers have been set aside until the experimental induction equipment is set up.

Projected Effort

In the forthcoming quarter, experiments in deposition of pyrolytic graphite ribbon upon iridium shall be pursued via resistance heating in the present quartz chamber apparatus.

The effects of boiling mercury upon the surface geometry of carbon and graphite yarns shall also be explored. It is hoped that dissolution by mercury of traces of carbon from the surfaces of fibers will provide a smoother, better substrate for pyrolytic graphite deposits.

The installation of the experimental induction furnace will facilitate attempts at evaporative growth of graphite whiskers. It is anticipated that carbon, evaporating from the susceptor, may feed a growing whisker. This growth may be stimulated by appropriate applications of stress to encourage carbon atom migration to nucleation sites.

Another approach in the heating of filaments passing through a heated susceptor will be simultaneously to apply tensile stress, proving an aligning mechanism to enhance filament strength.

References

No.

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3. F.E. Papalegis and R. G. Bourdeau, "Pyrolytic Reinforcing Agents for Ablative Erosion-Resistant Composites", ASD-TDR-63-403, May 1963.

4. Higgs, Finicle, Bobka, Seldin & Zeitsch, "Research and Development on Advanced Graphite Materials, Vol. XXXVII – Studies of Graphite Deposited by Pyrolytic Processes" WADD TR61-72, May 1964.

5. W.A. Robba Pyrogenics personal communication, 1964.

6. L.A. Yerkovitch and H.P. Kirchner, "Growth and Mechanical Properties of Filamentary Silicon Carbide Crystals", WADD TR61-252, June 1962.

7. A. Gatti, R. Cree, E. Feingold, R. Mehan, "The Synthesis of Boron Carbide Filaments" N64-24112, Third Quarterly Report, April 10, 1964.
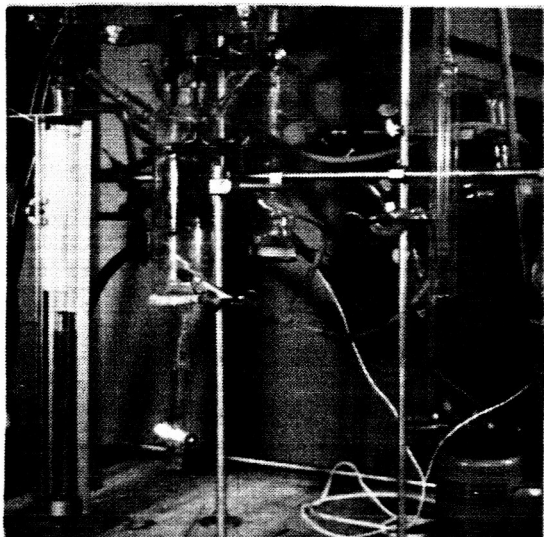
Figure 1
Vacuum and atmospheric heating
apparatus
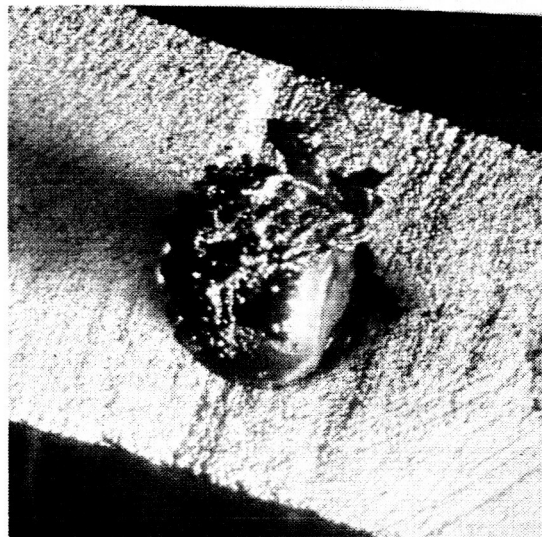
Figure 2
Platinum with irregular pyrolytic deposit,
in graphite boat (10x)

Figure 3
Pyrolytic deposit on platinum (40x)
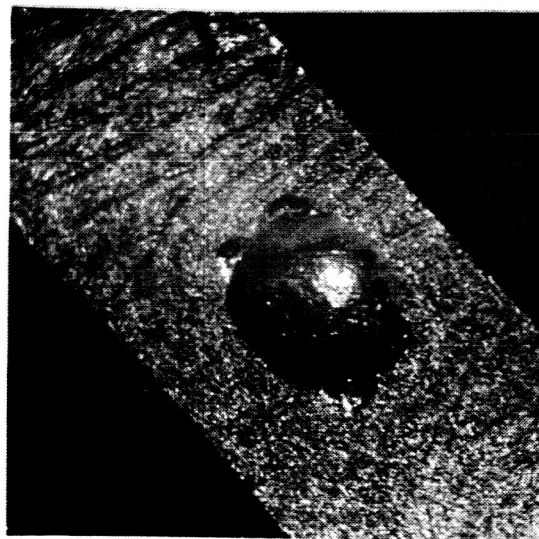
Figure 4
Light, wrinkled-deposit over molten
platinum, partially peeled (10x)

Figure 5   40x
Wrinkled deposit over molten platinum

Figure 6
Wrinkled pyrolytic deposits overlying
precipitated graphite layer.
(300x, 2-A-2-1).
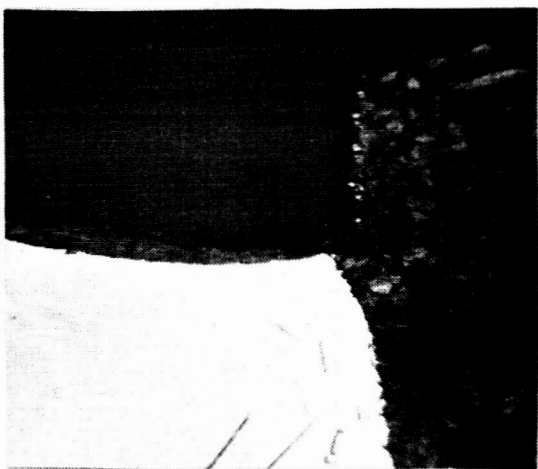
Figure 7
Precipitated graphite film (center)
over platinum. Graphite boat
(right). 300x, 5-A-5-1).
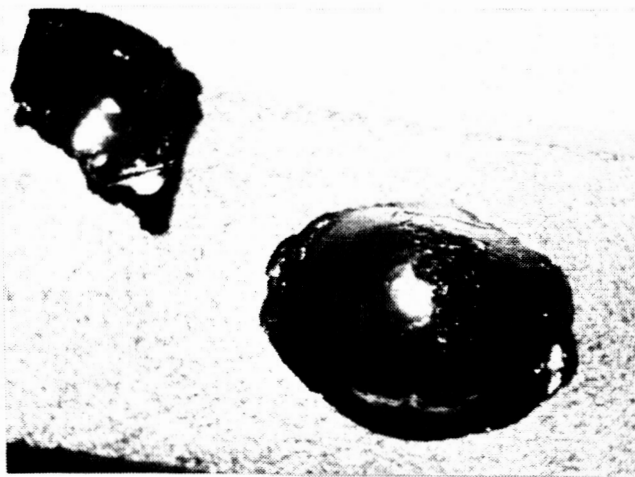
Figure 8
Smooth PG deposit over molten platinum.
Flake (left) lifted from right side of
cooled melt (10x).
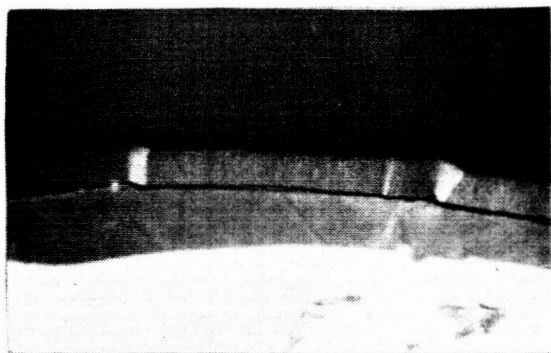
Figure 9
Pyrolytic, oven precipitated graphite
on platinum melt (300x, 3-A-3-1).
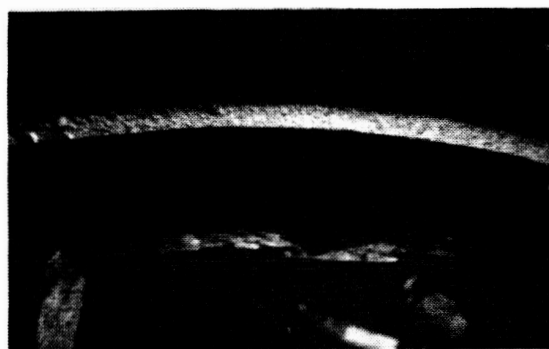
Figure 10
Pyrolytic graphite, displaced from platinum
and precipitated graphite (150x, 6-A-6-1)
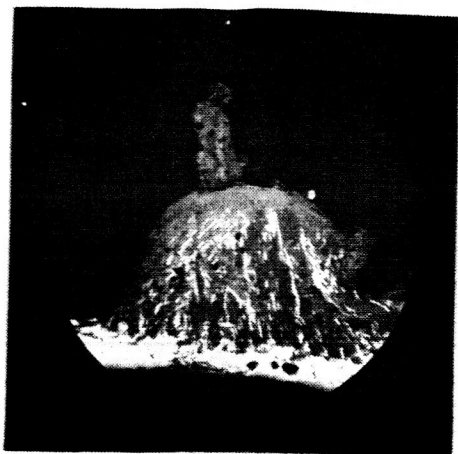
Figure 11
Irregular PG deposit over
large transferred graphite
mass in platinum melt.
10x, 1-A-1-1).
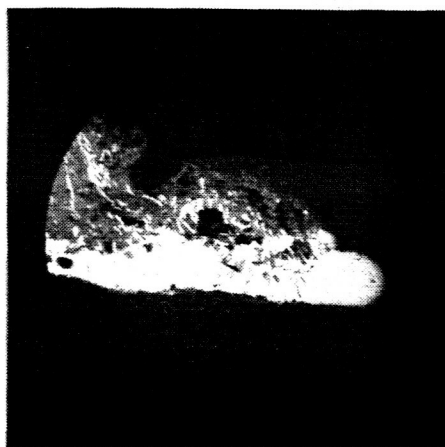
Figure 12
Penetration of graphite
boat by platinum melt,
through center line
(10x, 1-A-1-2)
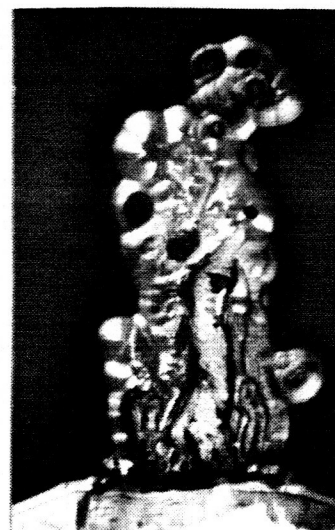
Figure 13
PG deposit (55x,
1-A-1-3).
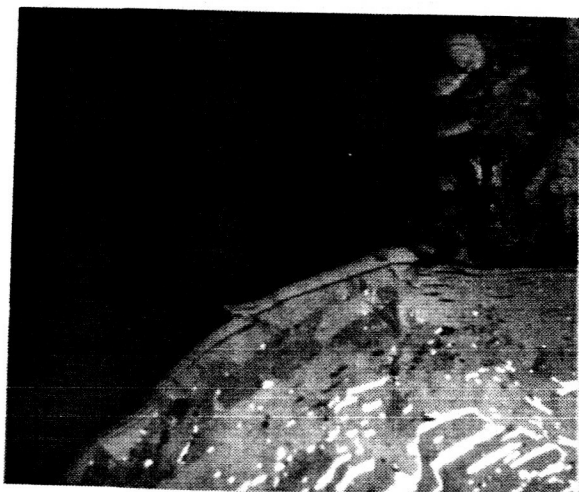
Figure 14
Irregular PG and more recent, less
distorted deposit, left (75x, 1-A-1-4)
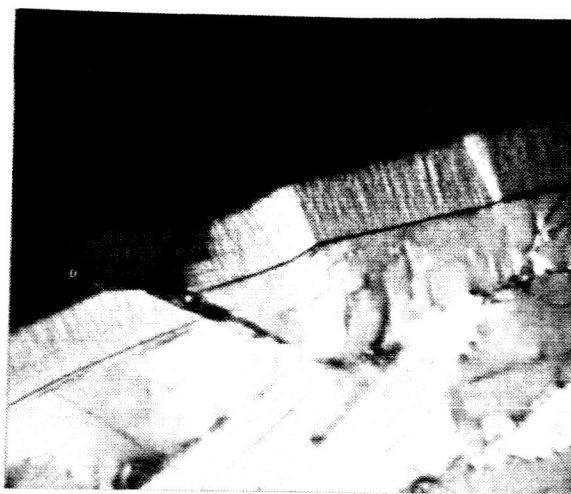
Figure 15
PG texture, versus underlying
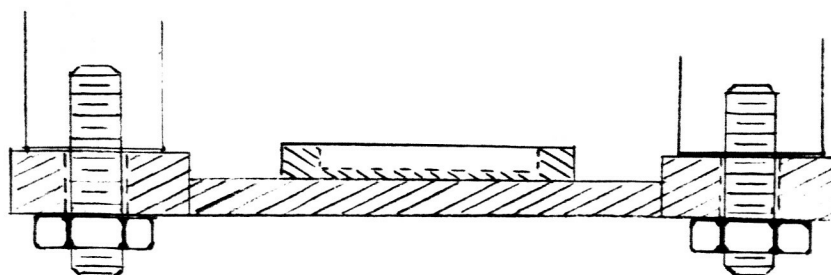precipitated graphite
(300x, 1-A-1-6)

Figure 16
Resistance heated graphite element between cooled
graphite electrodes, supporting graphite boat.
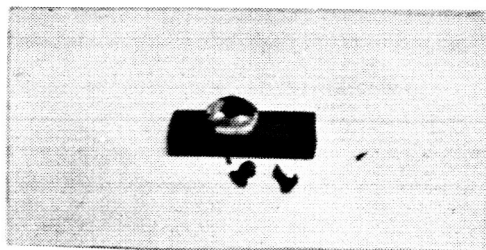
Figure 17
Non-wetting copper melt in graphite
boat, with a portion of deposit
removed.

Figure 18
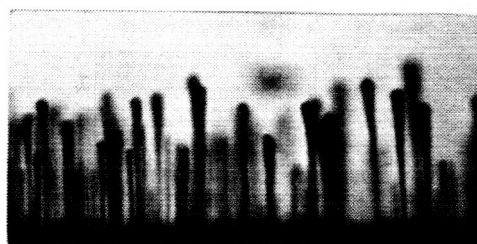Whisker growth on graphite heating
element (10x).
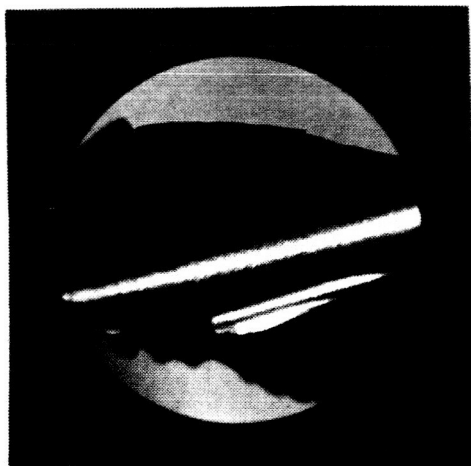

Figure 19
Whiskers (40x)

Figure 20
Pyrolytic foil grown on
rhenium (5x, 4-A-4-0)

Figure 21
Section of pyrolytic graphite foil,
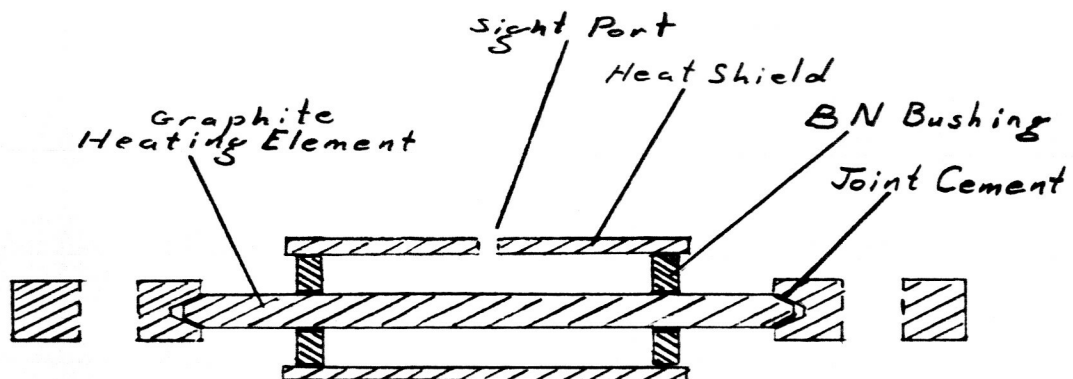peeled from rhenium ribbon.
(150x, 4-A-4-3)

Figure 22
Resistance heated graphite element, graphite shield, and supporting boron nitride bushings.
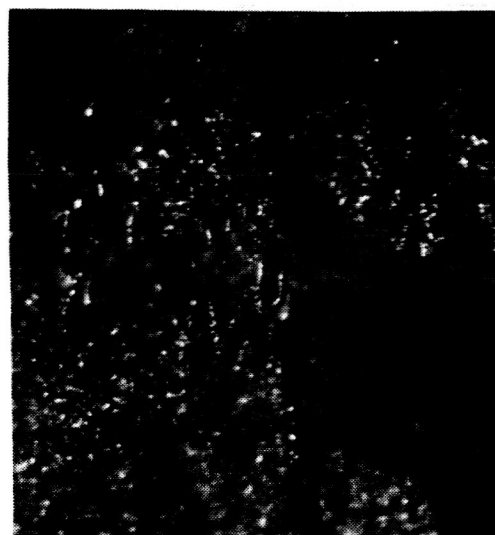

Figure 23
Carbide deposit on boron nitride vushings. (10x)

Figure 24
Carbide whiskers (40x)